Indicator: Nitrogen and Phosphorus Discharge from Large Rivers (146)

Nitrogen is a critical nutrient for plants and animals, and terrestrial ecosystems and headwater streams have a considerable ability to capture nitrogen or to reduce it to N_2 gas though the process of denitrification. Nitrogen cycling and retention is thus one of the most important functions of ecosystems (Vitousek, et al., 2002). When loads of nitrogen from fertilizer, septic tanks, and atmospheric deposition exceed the capacity of terrestrial systems (including croplands), the excess may enter surface waters, where it may have “cascading” harmful effects as it moves downstream to coastal ecosystems (Galloway and Cowling, 2002). Other sources of excess nitrogen include direct discharges from storm water or treated wastewater. This indicator specifically focuses on nitrate, which is one of the most bioavailable forms of nitrogen in bodies of water.

Phosphorus is a critical nutrient for all forms of life, but like nitrogen, phosphorus that enters the environment from man-made sources may exceed the needs and capacity of the terrestrial ecosystem. As a result, excess phosphorus may enter surface waters. Unlike nitrogen – which affects water quality primarily downstream, in coastal waters – the effects of excess phosphorus can be seen directly in lakes and streams. Because phosphorus is often the limiting nutrient in these bodies of water, an excess may contribute to unsightly algal blooms, which cause taste and odor problems and deplete oxygen needed by fish and other aquatic species. The most common sources of phosphorus in rivers are fertilizer and wastewater, including storm water and treated wastewater discharged directly into the river. In most watersheds, the atmosphere is not an important source or sink for phosphorus.

This indicator tracks trends in the discharges of nitrate and phosphorus from the four largest rivers in the United States: the Mississippi, Columbia, St. Lawrence, and Susquehanna. While not inclusive of the entire nation, these four rivers account for approximately 55 percent of all freshwater flow entering the ocean from the lower 48 states. This indicator relies on stream flow and water-quality data collected by the U.S. Geological Survey (USGS), which has monitored nitrate export from the Mississippi River since the mid-1950s and from the Susquehanna, St. Lawrence, and Columbia Rivers since the 1970s. Data were collected near the mouth of each river except the St. Lawrence, which was sampled near the point where it leaves the United States.

At the sites for which data are included in this indicator, USGS recorded daily stream levels and volumetric discharge using permanent stream gauges. Water quality samples were collected at least quarterly over the period of interest, in some cases up to 15 times per year. USGS calculated annual nitrogen load from these data using regression models relating nitrogen concentration to discharge, day-of-year (to capture seasonal effects), and time (to capture any trend over the period). These models were used to make daily estimates of concentrations, which were multiplied by the daily average discharge to yield the daily load (The Heinz Center, 2003). Because data on forms of nitrogen other than nitrate and nitrite are not as prevalent in the historical record, this indicator only uses measurements of nitrate plus nitrite. As nitrite concentrations are typically insignificant relative to nitrate, this mixture is simply referred to as nitrate.

What the Data Show

The Mississippi River, which drains more than 40 percent of the area of the lower 48 states, carries roughly 15 times more nitrate than any other U.S. river. Nitrate discharge from the Mississippi increased noticeably over much of the last half-century, rising from 200,000–500,000 tons per year in the 1950s and 1960s to an average of about 1,000,000 tons per year during the 1980s and 1990s (Figure 146-1). Large year-to-year fluctuations are also apparent. The Mississippi drains the agricultural center of the nation and contains a large percentage of the growing population, so it may not be surprising that the watershed has not been able to assimilate the nitrogen applied to crops and lawns, animal manures, nitrogen deposited from the atmosphere, and nitrogen deriving from human wastes (e.g., Rabalais and Turner, 2001).

The nitrate load in the Columbia River increased to almost twice its historical loads during the later half of the 1990s, but by the last year of record (2002), the amount of nitrate discharged had returned to levels similar to those seen in the late 1970s (Figure 146-1). The St. Lawrence River showed an overall upward trend in nitrate discharge over the period of record, while the Susquehanna does not appear to have shown an appreciable trend in either direction.

The amount of phosphorus discharged decreased in the St. Lawrence and Susquehanna Rivers over the period of record (Figure 146-2). There is no obvious trend in the Mississippi and Columbia Rivers, and the year-to-year variability is quite large. Nitrogen and phosphorus discharges tend to be significantly higher during years of high runoff, because of increased erosion and transport of the nutrients to stream channels (Smith et al., 2003).

Indicator Limitations

- The indicator does not include data from numerous coastal watersheds whose human populations are rapidly increasing (e.g., Valigura, et al., 2000).

- It does not include smaller watersheds in geologically sensitive regions, whose ability to retain nitrogen might be affected by acid deposition (e.g., Evans, et al., 2000).

- It does not include forms of nitrogen other than nitrate. Although nitrate is one of the most bioavailable forms of nitrogen from an ecological standpoint, other forms may constitute a substantial portion of the nitrogen load. Historically, nitrate data are more extensive than data on other forms of nitrogen.

- Not all forms of phosphorus included in the total phosphorus loads are equally capable of causing algal blooms.

Data Sources

Data for this indicator were collected and analyzed by USGS. Indicator derivation (project, program, organization, report): USGS, NASQAN and NAWQA programs, and the USGS Federal-State Cooperative Program. USGS data web site: http://waterdata.usgs.gov/nwis/. Additional data and modeling of recent nitrogen loads in the Mississippi and Columbia may be obtained from USGS's NASQAN website: http://water.usgs.gov/nasqan.

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Smith, S., et al. 2003. Humans, Hydrology, and the Distribution of Inorganic Nutrient Loading to the Ocean. BioScience 53: 235-245.

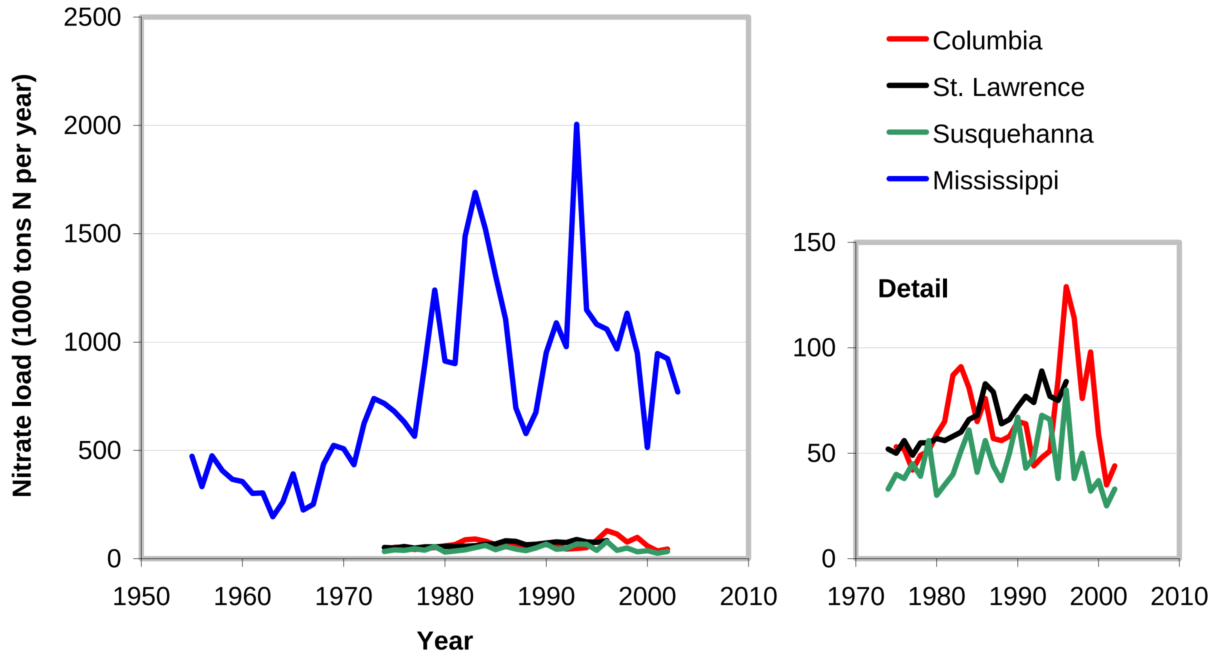
The H. John Heinz III Center for Science, Economics, and the Environment. 2003. The State of the Nation's Ecosystems: Measuring the Lands, Waters, and Living Resources of the United States. New York, NY: Cambridge University Press, September 2002. Web update 2003: http://www.heinzctr.org/ecosystems.

Valigura, R., R. Alexander, M. Castro, T. Meyers, H. Paerl, P. Stacey, and R. Turner (eds.). 2000. Nitrogen Loading in Coastal Water Bodies – An Atmospheric Perspective. Washington, DC: American Geophysical Union.

Vitousek, P., H. Mooney, L. Olander, and S. Allison. 2002. Nitrogen and nature. Ambio 31: 97-101.

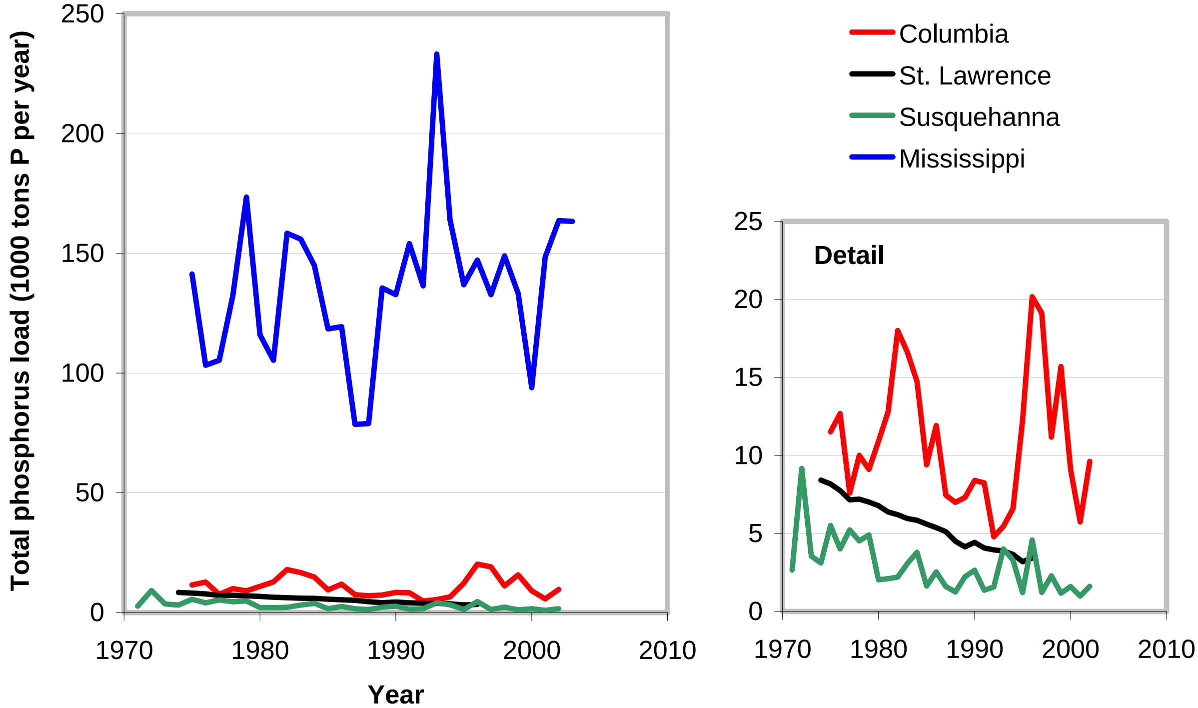
Graphics

Figure 146-1: Nitrate discharge from major rivers*



* Most of the measurements used for this indicator include nitrate plus nitrite. However, concentrations of nitrite are typically insignificant relative to nitrate; thus, the mixture is simply called "nitrate."

Figure 146-2: Total phosphorus discharge from major rivers



R.O.E. Indicator QA/QC

Data Set Name: NITROGEN AND PHOSPHORUS DISCHARGE FROM LARGE RIVERS
Indicator Number: 146 (89665)
Data Set Source: U.S. Geologic Survey
Data Collection Date: variable: 1955-2003
Data Collection Frequency: variable
Data Set Description: Nitrogen and Phosphorus Discharge from Large Rivers
Primary ROE Question: What are the trends in extent and condition of fresh surface waters in the United States?

Question/Response

T1Q1 Are the physical, chemical, or biological measurements upon which this indicator is based widely accepted as scientifically and technically valid?

This indicator is based on two main sets of field measurements: streamflow characteristics (depth and flow rate) and water quality (concentration of nitrate and total phosphorus). Data were collected following standard USGS sample collection and processing protocols. Streamflow measurements are described in several USGS procedural manuals, which can be found online at http://water.usgs.gov/pubs/twri/. Field collection protocols for water quality samples are documented by Horowitz et al. (1994) [full citation below], as well as at http://water.usgs.gov/pubs/twri/. For water quality data, protocols include standard sample collection methods. Samples are analyzed at the USGS National Water Quality Laboratory in Denver, CO, and nutrient concentrations reported in units of milligrams per liter. Specific laboratory methods for recent (1996-) measurements are documented online at http://water.usgs.gov/nasqan/progdocs/wri014255/methods.dat, and complete citations for these methods can be found online at http://water.usgs.gov/nasqan/progdocs/wri014255/refs.htm. For water quality data collected between 1973 and 1995, field and laboratory methods are cited by USGS at http://water.usgs.gov/pubs/dds/wqn96cd/. According to Goolsby et al. (1999), USGS has measured nitrate concentrations since 1970 using colorimetric cadmium reduction (Fishman and Friedman, 1989). Pre-1970 nitrate levels were measured using the corimetric phenoldisulfonic acid method (Rainwater and Thatcher, 1960). Concentrations of total phosphorus were measured using Microkjeldahl digestion (EPA method 365.1; see EPA, 1993). Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994. U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 pp. Goolsby, Donald A., William A. Battaglin, Gregory B. Lawrence, Richard S. Artz, Brent T. Aulenbach, Richard P. Hooper, Dennis R. Keeney, and Gary J. Stensland. 1999. Flux and Sources of Nutrients in the Mississippi-Atchafalaya River Basin: Topic 3 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 17. NOAA Coastal Ocean Program, Silver Spring, MD. 130 pp. Fishman, M.J., and L.C. Friedman, eds. 1989. Methods for determination of inorganic substances in water and fluvial sediments. In Techniques of water-resources investigations of the United States Geological Survey. Chapter A1. Washington, DC. Rainwater, F.W., and L.L. Thatcher. 1960. Methods for collection and analysis of water samples. U.S. Geological Survey Water Supply Paper 1454. Washington, DC. U.S. EPA. 1993. Methods for the determination of inorganic substances in environmental samples: EPA/600/R-93/100.

T1Q2 Is the sampling design and/or monitoring plan used to collect the data over time and space based on sound scientific principles?

Because data for this indicator were collected following several different sampling plans, depending on time and location, it is hard to make a single definitive statement about the scientific validity of sample design. Nonetheless, the spatial coverage appears sufficient to characterize discharges from the four major rivers (i.e., monitoring and sampling near the mouth of each river). In general, temporal coverage seems sufficient as well, with discharge measurements taken several times a day and water quality measurements recorded several times per year over the course of at least 30 years. A basic summary of sample design follows: (1) Water depth and stream discharge were measured several times every day and reported as daily averages. USGS operates over 7,000 continuous monitoring stream gauges across the United States. This indicator incorporates flow measurements taken from 8 USGS and U.S. Army Corps of Engineers (USACE) stations near the mouths of the four major rivers. USGS's analytical model also incorporates lagged flow data from 5 USGS/USACE stations located upstream within the Mississippi River basin. A complete list of stations appears in T3Q1. (2) Water quality (nitrate and phosphorus) measurements come from samples taken at 7 USGS and USACE sampling locations, also listed in T3Q1. Some of these samples were taken at the same locations as discharge measurements; the others were taken nearby. For both discharge and water quality, USGS chose the stations that were most appropriate for measuring nitrogen and phosphorus load close to the mouth of the river -- or in the case of the St. Lawrence, near where the river leaves the United States. Susquehanna data come from two locations, one prior to 1979 and another thereafter. Totals for the Mississippi and Columbia both include data from more than one station, since additional stations were needed to characterize discharges and nutrients from a major upstream diversion (the Atchafalaya) and a major downstream tributary (the Willamette). The frequency of water quality sampling varied from year to year, as described below: From 1996 to 2000, water quality data for the Mississippi and Columbia Rivers were collected through USGS's National Stream Water Accounting Network (NASQAN) Program, described at http://water.usgs.gov/nasqan/progdocs/wri014255/backgrnd.htm. Under NASQAN, a total of 15 water quality samples were taken each year: 12 at predetermined intervals, and 3 reserved for unique events (e.g., extreme high or low flows). NASQAN's website notes that in certain locations, the twelve regular samples are not evenly distributed over time, suggesting that they may be intentionally biased towards a month or season when extreme flow is expected. NASQAN's 1996-2000 sample design is discussed in a 2001 report located online at http://water.usgs.gov/nasqan/progdocs/wri014255/: Kelly VJ, Hooper RP, Aulenbach BT, and Janet M. Concentrations and annual fluxes for selected water-quality constituents from the USGS National Stream Quality Accounting Network (NASQAN), 1996-2000. Water-Resources Investigations Report 01-4255. Reston, Virginia. 2001. NASQAN did not collect data from either the St. Lawrence or the Susquehanna after 1995, so recent data from these rivers must come from other sources within USGS, such as the National Water Quality Assessment (NAWQA), which has studied 51 watersheds since 1991 (http://water.usgs.gov/nawqa/studyu.html). USGS does not discuss the frequency or intervals of measurement at these locations. From 1973 to 1995, water quality measurements were conducted at hundreds of stations under the auspices of NASQAN. These stations are noted at http://water.usgs.gov/nasqan/progdocs/, and include all four of the rivers included in this indicator. This link also includes a general description of the program; a more detailed history of NASQAN can be found at http://water.usgs.gov/pubs/dds/wqn96cd/html/report/hiswqn.htm#NASQAN. Unlike the 1

T1Q3 Is the conceptual model used to transform these measurements into an indicator widely accepted as a scientifically sound representation of the phenomenon it indicates?

In its presentation of an earlier version of this indicator, the Heinz Center reports that water depth data are first converted to streamflow (volumetric discharge) by means of a rating curve. USGS typically establishes a unique rating curve for each measuring station, in order to find the relationship between depth and discharge that is appropriate given the geometry of the specific river bed in question. Several procedures for converting depth to discharge, including the rating curve method, are documented in USGS's data-collection manuals. These are available online at http://water.usgs.gov/pubs/twri/ (specific reference: Book 3, Chapter A10). Some USGS gauging stations are equipped with current meters that measure discharge directly. The Heinz Center (2003) does not discuss how much of their USGS discharge data may have come from direct versus indirect physical measurements, but it is possible to look up each of the relevant measuring stations (see T1Q2) in USGS's online site inventory to find a list of the equipment in use at each site (http://nwis.waterdata.usgs.gov/nwis/si). The Heinz Center describes the general basis for deriving average annual nutrient flux from the data set. A regression model relates nutrient concentrations and discharge values measured on the same day, and then uses this relationship to derive an annual flux figure based on a full year's worth of discharge data. The regression model is also designed to account for possible seasonal variations in nitrate/phosphorus concentration. USGS conducted this stage of the analysis using two regression models -- LOADEST and Cohn's ESTIMATOR. Both of these models are well documented in scientific publications (see T3Q1), and are accepted as a valid means of calculating annual solute load from a limited number of water quality measurements. USGS notes that annual Mississippi River nitrate fluxes prior to 1967 were not necessarily calculated using the Estimator regression model (Richard Coupe, personal communication, 2004). Instead, annual fluxes may have been calculated simply by calculating the average relationship between nitrate load and discharge, then extrapolating based on daily discharge data for the entire year.

T2Q1 To what extent is the indicator sampling design and monitoring plan appropriate for answering the relevant question in the ROE?

Nitrogen and phosphorus discharge from large rivers, with samples collected and measured as described in T1Q3, is considered a key indicator in assessing the nation's water resources. In a general sense, this indicator is relevant to the major question at hand -- namely, what are trends in extent and condition of fresh surface waters? Increased levels of nitrogen carried by rivers may indicate that nutrient cycling in upstream ecosystems is unable to handle the volume of additional nitrogen added to the environment by human activities. This not only represents an overload upstream (Vitousek, et al., 2002), but also poses a threat downstream and offshore, where excess nitrogen is linked to eutrophication, hypoxia, and other potential threats to coastal ecosystems (Galloway and Cowling, 2002). Nitrate is generally the most bioavailable form of nitrogen in large rivers. Excess phosphorus has a more direct effect in lakes and streams, where phosphorus is often the limiting nutrient for plant growth. When these water bodies become overloaded with phosphorus, it can contribute to algal blooms that deplete oxygen needed by fish and other species (U.S. EPA, 1998). These algal blooms may also give the water an unappealing appearance, taste, or odor. Galloway, J., and E. Cowling. 2002. Reactive nitrogen and the world: 200 years of change. Ambio 31:64-71. U.S. EPA. 1998. National Strategy for the Development of Regional Nutrient Criteria: EPA 822-R-98-002. Washington, DC: U.S. Environmental Protection Agency, Office of Water, June 1998. Vitousek, P., H. Mooney, L. Olander, and S. Allison. 2002. Nitrogen and nature. Ambio 31:97-101. This indicator is designed to examine four major U.S. rivers (Mississippi, Columbia, St. Lawrence, and Susquehanna), which together carry over 50 percent of freshwater flow from the lower 48 states to the ocean (Heinz Center, 2003). Sample size is sufficient; 30 years of annual data are available for comparison among the four rivers, as well as nearly 50 years of data to aid in the analysis of longer-term nitrate trends in the Mississippi River. Streamflow and water quality were measured from at least one station near the mouth of each of the four rivers; in some cases, additional stations were used to capture contributions from important tributaries or diversion channels. Depth and discharge were measured several times a day, and while nitrate and phosphorus concentrations were typically measured 15 or fewer times each year, USGS's regression models are designed to estimate an annual load that accounts for daily and seasonal variation.

T2Q2 To what extent does the sampling design represent sensitive populations or ecosystems?

Focusing on the functional implications of nitrogen loss, this indicator is more of a holistic measure of ecosystem "overloading," rather than a detailed assessment of a particular risk factor to sensitive populations or ecosystems. Because this indicator represents only four large rivers, it may not represent sensitive ecosystems or populations located in smaller watersheds. Nonetheless, this indicator might reveal that one or more of the four major watersheds -- or associated ecoregions -- may be of particular concern because of the degree to which their chemical cycling systems appear to have become overwhelmed by human inputs of nitrogen and phosphorus.

T2Q3 Are there established reference points, thresholds or ranges of values for this indicator that unambiguously reflect the state of the environment?

The Heinz Report does not present any baseline data on nitrate or phosphorus flux that unambiguously reflect the state of the environment. The earliest data presented in this indicator date back to the mid-1950s, and while nitrate fluxes in most rivers have risen greatly since that time, it is still inaccurate to say that the 1950s nitrate fluxes represent background values for the natural, undisturbed state of the environment. In the United States, inorganic nitrogen fertilizer was in wide use by the 1950s, and the other major contributor to excess nitrate load -- atmospheric deposition -- was already occurring due to burning of fossil fuels (Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution. Commission on Geosciences, Environment and Resources (CGER), Ocean Studies Board (OSB), 2000. pp.113-162. http://books.nap.edu/books/0309069483/html/113.html). Similarly, it is unlikely that the earliest phosphorus data represent any sort of unambiguous baseline. Thus, this indicator is most useful for year-to-year or decade-to-decade comparisons.

T3Q1 What documentation clearly and completely describes the underlying sampling and analytical procedures used?

(1) Sampling and laboratory methods are thoroughly documented by USGS.
Field collection protocols for stream gauging are described in USGS procedural manuals available online through http://water.usgs.gov/pubs/twri/:

> Depth (stage) gauging: http://water.usgs.gov/pubs/twri/twri3-A6/ and http://water.usgs.gov/pubs/twri/twri3a7/
>
> Conversion of depth to discharge: http://water.usgs.gov/pubs/twri/twri3-a1/ and http://water.usgs.gov/pubs/twri/twri3-a10/
>
> Direct measurement of discharge: http://water.usgs.gov/pubs/twri/twri3a8/

The Heinz Center does not report using direct measurements of stream discharge, but USGS reports that current meters are in use at certain gauging stations. A full inventory of USGS gauging stations is available at http://nwis.waterdata.usgs.gov/nwis/si. Regardless of collection method, all streamflow data are available from USGS in the form of daily discharge measurements.

This indicator directly incorporates streamflow data from eight USGS and U.S. Army Corps of Engineers (COE) stations:

*** USGS 14105700 COLUMBIA RIVER AT THE DALLES,OREG.
*** USGS 14211720 WILLAMETTE RIVER AT PORTLAND,OREG.
*** USGS 04264331 ST. LAWRENCE R AT CORNWALL ONT NR MASSENA NY
*** USGS 01570500 SUSQUEHANNA RIVER AT HARRISBURG, PA
*** USGS 01578310 SUSQUEHANNA RIVER AT CONOWINGO, MD
*** Atchafalaya River At Simmesport, LA (07381495; COE 03045)
*** Mississippi River At Tarbert Landing, MS (07373420; COE 01100)
*** Old River Outflow Channel near Knox Landing, LA (Total Outflow; COE 02600)

These stations represent the best available stations to characterize discharge from the mouth of the river -- or in the case of the St. Lawrence, discharge near the point where the river leaves the United States. Due to the nature of gauge placement, total discharge figures for the Mississippi and Columbia require data from multiple gauges. For the Mississippi, additional gauges are located along major outflow channels (e.g., the Atchafalaya); measurements for the Columbia include flow from the Willamette, which empties into the Columbia downstream from the main stream gauge at The Dalles. Data for the Susquehanna came from Harrisburg until 1978 because data from Conowingo, further downstream, were not available until 1979.

In addition, the USGS models incorporated "lagged upstream flows" from five additional gauging stations (USGS, personal communication from Richard Coupe, 2004):

*** 05587455 Mississippi River at Grafton, IL
*** 07022000 Mississippi River at Thebes, IL
*** 03612500 Ohio River at Lock and Dam 53 near Grand Chain, IL
*** 06934500 Missouri at Hermann, MO
*** 07355500 RED R @ ALEXANDRIA, LA

(2) Water quality (nitrate and phosphorus) measurements come from samples taken at the following seven USGS and COE stations:

*** USGS 01570500 SUSQUEHANNA RIVER AT HARRISBURG, PA
*** USGS 01578310 SUSQUEHANNA RIVER AT CONOWINGO, MD
*** USGS 04264331 ST. LAWRENCE R AT CORNWALL ONT NR MASSENA NY
*** USGS 14128910 COLUMBIA RIVER AT WARRENDALE,OREG.
*** USGS 14211720 WILLAMETTE RIVER AT PORTLAND,OREG.
*** Lower Atchafalaya River at Melville, Louisiana (07381495; COE)
*** Mississippi River at St. Francisville, Louisiana (07373420; COE)

These stations do not all correspond exactly with the stream gauging stations listed above, but location differences are not significant. As with discharge measurements, nutrient data from multiple stations must be added to derive total figures for the Mississippi and Columbia.

Field collection protocols for water quality are documented in Horowitz et al. (1994) [full citation below] and in several procedural manuals located online at http://water.usgs.gov/pubs/twri/. These references discuss many aspects of sample collection, such as how to collect the sample (e.g., by boat), and in what part of the river. One manual specifically discusses how to adjust measured concentrations so they are representative of the entire cross-section of the river: http://water.usgs.gov/owq/FieldManual/Chapter6/6.0.2.html#HDR6.0.2.A.

Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 pp.

Water samples were tested for dissolved nitrate and total phosphorus. In some cases, the final "nitrate" figure also included nitrite (USGS, Richard Coupe, personal communication, 2004); however, the Heinz Center (2003) notes that nitrite concentrations are typically insignificant compared to nitrate. Specific laboratory methods for recent NASQAN samples (1996-) are documented at http://water.usgs.gov/nasqan/progdocs/wri014255/methods.dat, and complete citations for laboratory methodology can be found online at http://water.usgs.gov/nasqan/progdocs/wri014255/refs.htm. Additional information on NASQAN sampling and analytical procedures from 1973 to 1995 can be found at http://water.usgs.gov/pubs/dds/wqn96cd/. According to Goolsby et al. (1999), USGS has measured nitrate concentrations since 1970 using colorimetric cadmium reduction (Fishman and Friedman, 1989). Pre-1970 nitrate levels were measured using the corimetric phenoldisulfonic acid method (Rainwater and Thatcher, 1960). Concentrations of total phosphorus were measured using Microkjeldahl digestion (EPA method 365.1; see U.S. EPA, 1993).

> Goolsby, Donald A., William A. Battaglin, Gregory B. Lawrence, Richard S. Artz, Brent T. Aulenbach, Richard P. Hooper, Dennis R. Keeney, and Gary J. Stensland. 1999. Flux and Sources of Nutrients in the Mississippi-Atchafalaya River Basin: Topic 3 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 17. NOAA Coastal Ocean Program, Silver Spring, MD. 130 pp.
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> Fishman, M.J., and L.C. Friedman, eds. 1989. Methods for determination of inorganic substances in water and fluvial sediments. In *Techniques of water-resources investigations of the United States Geological Survey*. Chapter A1. Washington, DC.
>
> Rainwater, F.W., and L.L. Thatcher. 1960. *Methods for collection and analysis of water samples*. U.S. Geological Survey Water Supply Paper 1454. Washington, DC.

U.S. EPA. 1993. Methods for the determination of inorganic substances in environmental samples: EPA/600/R-93/100.

(3) USGS estimated the annual flux of nitrate and phosphorus using regression models. Nutrient loads in the Mississippi River were estimated using a model known as Cohn's "ESTIMATOR" code, applying an equation described in Goolsby et al (1999) [see citation in T1Q1]. Recent updates to this model are described at http://co.water.usgs.gov/hypoxia/html/nutrients_new.html ("USGS, 2004, New nutrient flux estimates for 2004"). The following three sources offer documentation of the ESTIMATOR model; the first two provide a theoretical basis, while the third offers a more hands-on explanation and application;

> Cohn, T.A., Delong, L.L., Gilroy, E.J., Hirsch, R.M., and Wells, D.K., 1989. Estimating constituent loads: Water Resources Research, 25(5):937-42.

Gilroy, E.J., Hirsch, R.M., and Cohn, T.A., 1990. Mean square error of regression-based constituent transport estimates: Water Resources Research, 26(9):2069-77.

Cohn, T.A., Caulder, D.L., Gilroy, D.J., Zynjuk, L.D., and Summers, R.M., 1992. The validity of a simple statistical model for estimating fluvial constituent loads: An empirical study involving nutrient loads entering Chesapeake Bay: Water Resources Research 28(9):2353-63.

In the other three rivers, USGS estimated nitrate and phosphorus loads using the LOADEST model, a similar regression tool. This model is described in Runkel et al (2004).

Runkel, R.L., Crawford, C.G., and Cohn, T.A. 2004. Load Estimator (LOADEST): A FORTRAN Program for Estimating Constituent Loads in Streams and Rivers: U.S. Geological Survey Techniques and Methods Book 4, Chapter A5, 69 p.

According to USGS (Richard Coupe, personal communication, 2004), pre-1967 nitrate concentrations were measured from 10-to-30-day composite samples. Annual flux figures for this period were extrapolated using daily discharge data and the relationship between discharge and solute flux that was evident from the composite nitrate samples. USGS may only have used the ESTIMATOR model on data from 1967 and later, which represents a possible source of inconsistency in the Mississippi River data series.

T3Q2 Is the complete data set accessible, including metadata, data-dictionaries and embedded definitions or are there confidentiality issues that may limit accessibility to the complete data set?

USGS provides free access to daily discharge data covering the entire sampling period for this indicator (http://waterdata.usgs.gov/nwis/sw). These are the raw data used by USGS in its analysis. In some cases, discharge data were originally derived from stream level measurements, which are also available from the same website. In a few cases, streamflow data were analyzed by USGS's National Stream Water Accounting Network (NASQAN) but obtained from gauges operated by the U.S. Army Corps of Engineers (USACE), not by USGS. Data from USACE stream gauges are included in NASQAN's database, which can be found at http://water.usgs.gov/nasqan/data/index.html. Water quality data (nitrate and phosphorus) are available through USGS's NWIS database (http://waterdata.usgs.gov/nwis/qw), and are also published in annual reports by state. Data used to derive this indicator can be obtained from NWIS by entering the identification numbers of the gauging and sampling stations listed in T3Q1. The data compilation that USGS created for this indicator has not been published, but could be obtained by contacting USGS directly (Bill Wilber, USGS, personal communication, 2005). USGS did publish historical nutrient flux data for the Mississippi River in a 1999 report by Goolsby et al. (citation below). Goolsby, Donald A., William A. Battaglin, Gregory B. Lawrence, Richard S. Artz, Brent T. Aulenbach, Richard P. Hooper, Dennis R. Keeney, and Gary J. Stensland. 1999. Flux and Sources of Nutrients in the Mississippi-Atchafalaya River Basin: Topic 3 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 17. NOAA Coastal Ocean Program, Silver Spring, MD. 130 pp.

T3Q3 Are the descriptions of the study or survey design clear, complete and sufficient to enable the study or survey to be reproduced?

Reproducibility of individual measurements is limited by the fact that this indicator relies largely on historical data. However, the list of gauging and sampling stations provided in T3Q1 facilitates easy access to all the online USGS data necessary to reproduce this study. Using the regression models documented in T3Q1, it should be possible to reproduce the full analysis that went into the creation of this indicator.

T3Q4 To what extent are the procedures for quality assurance and quality control of the data documented and accessible?

The Heinz Center does not directly document quality control procedures for this indicator, but several relevant USGS references are available online. For discharge measurements, see Sauer and Meyer, "Determination of error in discharge measurements," located at http://pubs.er.usgs.gov/pubs/ofr/ofr92144. Another useful USGS resource is: Rantz et al., "Measurement and computation of streamflow: volume 1. Measurement of stage and discharge," located at http://water.usgs.gov/pubs/wsp/wsp2175/pdf/WSP2175_vol1a.pdf. General QA/QC procedures for water quality measurements associated with USGS's NASQAN Program are well documented. NASQAN outlines several general QA/QC procedures at http://water.usgs.gov/nasqan/progdocs/wri014255/methods.htm, while an additional assessment of field sampling quality control procedures can be found at http://water.usgs.gov/nasqan/progdocs/wri014255/results/qc.htm. Among other things, these documents discuss field blanks, replicates, and how outliers are treated when measuring solute concentration. Most of this information is specifically relevant to the sampling that took place under the auspices of NASQAN beginning in 1996. Quality assurance information for data sets prior to 1996 is available at http://water.usgs.gov/pubs/dds/wqn96cd/html/wqn/qasure/qasure.htm. This link includes a description of field and laboratory procedural changes that have occurred since the 1970s. In certain cases where procedures have not changed, the NASQAN QA/QC information may be applicable to data collected prior to 1996. Related information about NASQAN's Blind Sample Program (pre-1996 laboratory QA/QC) can be found at http://water.usgs.gov/pubs/dds/wqn96cd/html/wqn/bsp/bsp.htm.

T4Q1 Have appropriate statistical methods been used to generalize or portray data beyond the time or spatial locations where measurements were made (e.g., statistical survey inference, no generalization is possible)?

The major source of generalization in the indicator data set is the use of a regression model to calculate annual nitrate and phosphorus load. While discharge is measured on a daily basis, nitrate and phosphorus concentrations are not. The graphical representation of this indicator -- annual nitrate and phosphorus loads -- is based entirely on regression models that extrapolates from 4 to 15 water quality measurements made over the course of a given year. These models account for day-to-day variation by linking nutrient load to discharge volume, and accounts for other sources of potential variability (e.g., seasonal changes in the nitrogen cycle) by regressing around each data point. The Heinz Center (2003) reports that USGS's regression models employed "robust statistical techniques that made no assumption about the underlying statistical distribution of the data." A small degree of spatial generalization is inherent in the process of using river outflow to characterize the ecosystem health of an entire watershed. However, no attempt is made to portray data beyond the bounds of the four key watersheds measured as part of this study.

T4Q2 Are uncertainty measurements or estimates available for the indicator and/or the underlying data set?

USGS and the Heinz Center do not present exact figures for uncertainty in this indicator. However, as a general reference, USGS has published several guides for calculating uncertainty of discharge measurements (see "Determination of error in discharge measurements" by Sauer and Meyer, http://pubs.er.usgs.gov/pubs/ofr/ofr92144). In terms of a general range for uncertainty, Goolsby et al. (1999) notes that discharge measurements are typically within 10 percent of actual values, and that accuracy figures for individual stream gauges are published in annual USGS reports for each state (citation below). A general USGS resource on uncertainty in water sampling can be found at http://water.usgs.gov/pubs/twri/twri4a3/, but no specific uncertainty measurements are presented for this indicator data set. Uncertainties in laboratory measurements are described within USGS's procedural and quality control documents (see also T3Q1 and T3Q4). Although USGS has documented the number of stream gauging and water quality sampling sites used in this analysis, the fact that the number of water quality samples per year varied throughout the sample period (see T1Q2) makes it difficult to calculate uncertainty for this indicator. USGS has not reported the exact nature of any statistical uncertainty related to the regression model. Considering that 4 to 15 days of data are used to determine nutrient load figures for an entire year, one might expect uncertainty to be significant. However, USGS's regression models have been developed using many years of data, and are considered to provide at least a reliable estimation of load. Goolsby, Donald A., William A. Battaglin, Gregory B. Lawrence, Richard S. Artz, Brent T. Aulenbach, Richard P. Hooper, Dennis R. Keeney, and Gary J. Stensland. 1999. Flux and Sources of Nutrients in the Mississippi-Atchafalaya River Basin: Topic 3 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 17. NOAA Coastal Ocean Program, Silver Spring, MD. 130 pp.

T4Q3 Do the uncertainty and variability impact the conclusions that can be inferred from the data and the utility of the indicator?

USGS does not explicitly quantify all of the uncertainties related to sampling methods and regression modeling for this indicator, as discussed in T4Q2. However, the largest source of uncertainty is probably inconsistent sample design. Although nitrate data for this indicator has been collected since the 1950s (phosphorus since the 1970s), collection has taken place under the auspices of several different USGS programs, each with its own criteria for where, when, and how often to make measurements. Specific issues: " The lack of data quality information on nitrate data from the 1950s and 1960s. These early data are included in the graphic depicting Mississippi River nitrate loads, but little documentation is provided as to whether these data were measured using the same procedures employed in more recent years. These data predate USGS's procedural and quality control documents, and may even predate some of the laboratory methods that USGS now uses to quantify solute concentrations. According to USGS (Richard Coupe, personal communication, 2004), pre-1967 data for the Mississippi River were collected as 10-to-30-day composite samples, and annual fluxes during this period may have been calculated by extrapolation, not by regression (see T3Q1). " Changing frequency of data collection. Water quality data were collected under the auspices of NASQAN from 1973 to 1995. According to NASQAN's website, frequency of sampling dropped over this period as the program's funding decreased; by 1994, samples were taken on a quarterly basis (http://water.usgs.gov/nasqan/progdocs/index.html). From 1996 to 1999, a revamped NASQAN measured fewer sites, 15 times per year. " Different intervals of measurement. According to NASQAN (http://water.usgs.gov/nasqan/progdocs/index.html), prior to 1996, USGS measured solute concentrations at equal intervals throughout the year (e.g., monthly or quarterly). Beginning in 1996, the program timed most measurements to coincide with large "events" or extreme high or low flows. " Different programs in different locations. NASQAN provides information about the Mississippi and Columbia Rivers, but information on the St. Lawrence and

Susquehanna must be taken from other USGS water quality monitoring programs, such as NAWQA (National Water Quality Assessment). While sampling and QA/QC procedures are included in NASQAN's 2001 report (http://water.usgs.gov/nasqan/progdocs/wri014255/index.htm), similar information is not available at the same level of detail for NAWQA. A related concern is that the discharge and water quality station closest to the mouth of the Susquehanna, located at Conowingo, MD, did not begin collecting significant data until 1979. Data up to 1978 come from Harrisburg, PA, over 50 miles upstream. Daily and seasonal variability is inherent in discharge and solute flux data. USGS designed its regression models to capture this variability, incorporating the full range of daily and seasonal flow characteristics into an overall annual figure. Year-to-year variability is also inherent in this indicator. Nitrogen and phosphorus discharges tend to be significantly higher during years of high runoff, because of increased erosion and transport of the nutrients to stream channels (Smith et al., 2003). Thus, it is important not to read too much into inter-annual trends -- at least in terms of determining causation -- because these trends may be more attributable to climate variability than to any human influence. Smith, S., et al. 2003. Humans, Hydrology, and the Distribution of Inorganic Nutrient Loading to the Ocean. BioScience 53: 235-245.

T4Q4 Are there limitations, or gaps in the data that may mislead a user about fundamental trends in the indicator over space or time period for which data are available?

(1) Limited to four major rivers. This indicator does not include data from numerous coastal watersheds whose large or growing human populations may represent significant sources of excess nitrogen (e.g., Valigura, et al., 2000). It also does not include a number of small watersheds whose geological characteristics may make them particularly sensitive to nitrogen cycle disruption due to acid deposition (e.g., Evans et al., 2000). Valigura, R., R. Alexander, M. Castro, T. Meyers, H. Paerl, P. Stacey, and R. Turner (eds.). 2000. Nitrogen Loading in Coastal Water Bodies -- An Atmospheric Perspective. Washington, DC: American Geophysical Union. Evans, C.D., A. Jenkins, and R. F. Wright. 2000. Surface water acidification in the South Pennines I. Current status and spatial variability. Environmental Pollution 109(1): 11-20. (2) Limited to nitrate. This indicator does not include other forms of nitrogen, which may constitute a substantial portion of the total nitrogen load. The Heinz Center does present an alternative form of this indicator, nitrogen yield, in terms of total nitrogen lost per square mile of each watershed. These calculations are based on recent USGS water quality data that include nitrate, nitrite, ammonia, and organic nitrogen (a complete listing of nitrogen compounds included in the NAWQA database, 1991-present, can be found at http://water.usgs.gov/nawqa/constituents/nutrients.html). Total nitrogen yield is calculated using a series of regression models (Heinz Center, 2003). However, because nitrate-only measurements are available for a longer time period than total nitrogen data, the indicator is limited to nitrate only, thereby maximizing the temporal range of data available. (3) Does not break down "total phosphorus" into components. Some forms of phosphorus (e.g., phosphates) are more biologically active than others, and are therefore more worrisome from the perspective of preventing algal blooms.